


REC'D 20 NOV 2001

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference Case #1888		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/21874	International filing date (day/month/year) 10/08/2000	Priority date (day/month/year) 10/08/1999	
International Patent Classification (IPC) or national classification and IPC A61K7/00			
Applicant NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CO			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input checked="" type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input checked="" type="checkbox"/> Certain defects in the international application</li> <li>VIII <input type="checkbox"/> Certain observations on the international application</li> </ul>			
Date of submission of the demand  09/03/2001		Date of completion of this report  15.11.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  Georgopoulos, N  Telephone No. +49 89 2399 2634	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US00/21874

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):  
**Description, pages:**

1-85 as originally filed

**Claims, No.:**

1-13 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/21874

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## II. Priority

1. ☒ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:
- ☐ copy of the earlier application whose priority has been claimed.
  - ☒ translation of the earlier application whose priority has been claimed.
2. ☐ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid.

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes: Claims
	No: Claims 1-7, 9-13
Inventive step (IS)	Yes: Claims
	No: Claims 1-13
Industrial applicability (IA)	Yes: Claims 1-13
	No: Claims

2. Citations and explanations  
see separate sheet

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
see separate sheet

**Item II**

- 1 Up to the date of issue of the present Written Opinion, a translation of the present application's priority document has not been available. Therefore, the examination of said application will be carried out as if its priority were not validly claimed, which means that the relevance of documents WO-A-99 39688 and FR-A-2 782 636 (indicated as P-documents in the International Search Report) will be assessed as normal prior art.

**Item V**

- 2 Reference is made to the following documents:

D1: WO-A-99 39688

D2: FR-A-2 782 636

- 3 The subject-matter of present independent claim 1 as well as that of present dependent claims 2 to 7 and 9 to 13, is not new (Art.33 (3) PCT).

- 3.1 D1 discloses a skin care lotion comprising:

i/ an amphoteric urethane resin having one or more carboxyl groups and one or more tertiary amino groups in a single molecule; and  
ii/ polyoxyethylene(POE) dimethicone (see pages 7 to 8, example 1 and page 13, line 22 to page 14, line 8 of D1).

D2 discloses a hairstyling cosmetic composition comprising:

i/ an amphoteric urethane resin as in present claim 1; and  
ii/ a silicone partially or totally neutralized comprising a carboxylic function (see claims 1, 2, 3 and 7 of D2).

- 3.2 Thus, the subject-matter of present independent claim 1 is anticipated by any of D1 and D2.

- 3.3 Furthermore, D1 anticipates the subject-matter of present dependent claims 2, 3, 6, 7, 9, 10, 12 and 13 (see page 4, lines 17 to 20 and page 7, lines 6 to 12 of D1) and

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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D2 the subject-matter of present dependent claims 2 to 6, 9, 11 and 13 (see page 8, lines 10 to 21, page 10, lines 8 to 21 and 23 to 30, page 14, line 11 to page 15, line 8 and page 15, lines 10 to 13 and 15 to 23 of D2).

- 4 Even if the applicant establishes novelty for the subject-matter of present claim 1, it seems that an inventive step cannot be acknowledged (Art.33 (4) PCT), as present invention's technical contribution (see, e.g. page 59, lines 1 to 6 and page 84, line 17 to page 85, line 5 of the present description) has already been mentioned in D1 (closest prior art document; see page 1, lines 22 to 25, page 2, lines 15 to 21 and page 7, lines 3 to 5 of D1).
- 5 The subject-matter of present claims 1 to 13 is susceptible of industrial application in the field of cosmetics industry (Art.33 (4) PCT).

**Item VII**

- 6 Contrary to the requirements of Rule 5.1 (a) (ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>Case #1888</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 00/21874</b>	International filing date (day/month/year) <b>10/08/2000</b>	(Earliest) Priority Date (day/month/year) <b>10/08/1999</b>
Applicant  <b>NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CO</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**COSMETIC COMPOSITIONS CONTAINING AMPHOTERIC URETHANE RISINS AND SILICONE POLYMERS**

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

/US 00/21874

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WO 99 39688 A (TSUZUKI TOSHITAKA ;ASAOKA SEIJI (JP); KOYAMA KATSUYA (JP); SAKURAI)</p> <p>12 August 1999 (1999-08-12)</p> <p>page 1, line 2-5, 25-28</p> <p>page 2, line 1-5, 15-27</p> <p>page 3, line 3-5, 9-15</p> <p>page 6, line 19-22</p> <p>page 7, line 1-12</p> <p>examples 1-3</p> <p>table 6</p> <p>claims 1-6</p> <p style="text-align: center;">--- -/--</p>	1-3, 9, 13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

19 January 2001

Date of mailing of the international search report

19/02/2001

Name and mailing address of the ISA

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Authorized officer

Bazzanini, R

## INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	• FR 2 782 636 A (OREAL) 3 March 2000 (2000-03-03) page 1, line 1-8 page 2, line 9-15, 24-32 page 3, line 9-18 page 6, line 9-13 page 9, line 30 -page 13, line 7 claims 1-14, 19 ---	1, 3, 4, 6-13
A	• EP 0 619 111 A (NAT STARCH CHEM INVEST) 12 October 1994 (1994-10-12) page 6, line 35 -page 7, line 15 tables 3, 4 ---	1, 3, 4, 6-13
A	• FR 2 771 927 A (OREAL) 11 June 1999 (1999-06-11) page 3, line 1-9 page 4, line 9-16 page 4, line 27 -page 5, line 4 page 7, line 8-29 page 8, line 6 -page 12, line 20 claims 1-7, 11, 12, 16, 18 -----	1-13



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

US 00/21874

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9939688	A	12-08-1999	JP 11228363 A AU 2671999 A EP 1052970 A	24-08-1999 23-08-1999 22-11-2000
FR 2782636	A	03-03-2000	AU 5172999 A BR 9906740 A CN 1275068 T EP 1049445 A WO 0012056 A	21-03-2000 15-08-2000 29-11-2000 08-11-2000 09-03-2000
EP 0619111	A	12-10-1994	CA 2120644 A,C DE 69401230 D DE 69401230 T JP 6321741 A US 5626840 A	07-10-1994 06-02-1997 24-04-1997 22-11-1994 06-05-1997
FR 2771927	A	11-06-1999	BR 9805658 A CN 1233463 A EP 0925778 A JP 11236311 A PL 330106 A	11-04-2000 03-11-1999 30-06-1999 31-08-1999 07-06-1999

**PCT**

**NOTIFICATION OF ELECTION**

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 05 July 2001 (05.07.01)	
International application No. PCT/US00/21874	Applicant's or agent's file reference Case #1888
International filing date (day/month/year) 10 August 2000 (10.08.00)	Priority date (day/month/year) 10 August 1999 (10.08.99)
Applicant ASAOKA, Seiji et al	

1. The designated Office is hereby notified of its election made:

☒

in the demand filed with the International Preliminary Examining Authority on:

09 March 2001 (09.03.01)

☐

in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer H. Zhou Telephone No.: (41-22) 338.83.38
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(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
15 February 2001 (15.02.2001)

PCT

(10) International Publication Number  
**WO 01/10394 A2**

- (51) International Patent Classification<sup>7</sup>: **A61K 7/00** (74) Agents: DEC, Ellen, T. et al.; National Starch and Chemical Company, P.O. Box 6500, Bridgewater, NJ 08807 (US).
- (21) International Application Number: **PCT/US00/21874**
- (22) International Filing Date: **10 August 2000 (10.08.2000)** (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:  
11/226559 10 August 1999 (10.08.1999) JP (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION** [US/US]; P.O. Box 7663, Wilmington, DE 19803-7663 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ASAOKA, Seiji** [JP/JP]; 18-26-702, Kamiyamate-cho, Suita-shi, Osaka 565-0841 (JP). **KOYAMA, Katsuya** [JP/JP]; 5-4-1-202, Senzo, Itami-shi, Hyogo 664-0898 (JP). **TSUZUKI, Toshitaka** [JP/JP]; 3-7-46, Senba-nishi, Minoo-shi, Osaka 562-0036 (JP). **HASHIMOTO, Tomohiro** [JP/JP]; 2-10-3, Nishi-tada, Kawanishi-shi, Hyogo 666-0138 (JP).
- Published:**  
— *Without international search report and to be republished upon receipt of that report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **COSMETICS**

(57) Abstract: The present invention provides a cosmetic which is superior in both characteristics of feel and spread at the time of application. The cosmetic is a cosmetic comprising an amphoteric urethane resin having carboxyl group(s) and tertiary amino group(s) in a molecule, and a silicone polymer.

WO 01/10394 A2

## COSMETICS

### Field of the Invention

The present invention relates to cosmetics containing an amphoteric urethane resin and a silicone  
5 polymer.

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### Description of the Related Art

As a base resin for cosmetics such as hair fixatives, for example, water-soluble resins such as  
10 nonionic (non-ionic) polyvinyl pyrrolidone (PVP), cationic acrylic resin or cellulose, anionic acrylic resin or polyvinyl acetate, and amphoteric acrylic resin or polyvinyl acetate have hitherto been used. Hair fixatives comprising these water-soluble resins as the base resin  
15 have merits such as high curl holding power and excellent durability, but have problems such as poor touch, which is important for cosmetics, and drastically poor feel.

On the other hand, the present inventors found  
20 that an amphoteric urethane resin having carboxyl group(s) and tertiary amino group(s) in a molecule can provide excellent feel because of the elasticity and strong toughness of the urethane resin and filed a patent application with respect to a resin composition for  
25 cosmetics, comprising the amphoteric urethane resin as

the base resin (Japanese Patent Application No. Hei 10-27595).

However, the cosmetic comprising the amphoteric urethane resin as the base resin is superior in feel, but  
5 has such a problem that a friction coefficient of the surface is large and spread at the time of application is inferior because of poor surface smoothness.

#### Summary of the Invention

10 The present invention has been accomplished under these circumstances and an object thereof is to provide a cosmetic which is superior in both characteristics of touch and spread at the time of application.

15 To attain the object described above, the present invention is directed to a cosmetic comprising an amphoteric urethane resin having carboxyl group(s) and tertiary amino group(s) in a molecule, and a silicone polymer.

20 The present inventors have studied intensively to solve the problems such as surface smoothness, which is a weak point in case of using the amphoteric urethane resin. As a result, they have found that, when using an amphoteric urethane resin in combination with a silicone  
25 polymer, good results are obtained. That is, since the

compatibility of the said amphoteric urethane resin with the silicone polymer is not high and the silicone polymer has stronger hydrophobicity, the amphoteric urethane resin and silicone polymer cause micro phase separation and the silicone polymer is unevenly distributed on the surface, thereby making it possible to provide the surface with the smoothness. As a result, they have found that a cosmetic comprising the amphoteric urethane resin in combination with the silicone polymer is superior in spread at the time of application without impairing the touch when using the amphoteric urethane resin alone, thus completing the present invention.

When using an aqueous solution or a water dispersion of the silicone polymer as the silicone polymer, the compatibility with the amphoteric urethane resin is enhanced to some degree, thereby making it possible to prepare a cosmetic having good stability.

When a structural unit derived from ethylene oxide is introduced, as a nonionic hydrophilic component, into the structure of the amphoteric urethane resin, sufficient hydrophilicity can be obtained and the hair washability is particularly improved when using as a hair cosmetic.

By introducing polysiloxane bond(s) into the structure of the said amphoteric urethane resin, the touch is further improved when using as a hair cosmetic.

### Description of the Preferred Embodiments

The embodiments of the present invention will now be described below.

The cosmetics of the present invention can be  
5 obtained by using an amphoteric urethane resin having  
carboxyl group(s) and tertiary amino group(s) in a  
molecule, and a silicone polymer.

The cosmetics of the present invention are used  
as hair cosmetics such as foam hair fixative, gel-like hair  
10 fixative, aerosol spray hair fixative, pump spray hair  
fixative and creamy hair fixative; skin care cosmetics  
such as shaving cream, skin care lotion and sunscreen  
lotion; and make-up cosmetics such as nail polish,  
mascara and foundation; and are particularly preferably  
15 used as hair cosmetics.

The amphoteric urethane resin having carboxyl  
group(s) and tertiary amino group(s) in a molecule can be  
prepared, for example, by reacting a polyol compound  
(component A), a polyisocyanate compound (component  
20 B) and a compound having active hydrogen(s) and  
carboxyl group(s) (component C) in the presence of  
excess isocyanate groups to form an isocyanate group-  
containing prepolymer, and reacting the isocyanate  
group-containing prepolymer with a compound having  
25 active hydrogen(s) and tertiary amino group(s)

(component D). Alternatively, the amphoteric urethane resin can also be prepared by replacing the sequence of the reaction between the above specific components C and D, that is, by reacting the above components A, B, and D in the presence of excess isocyanate groups to form an isocyanate group-containing prepolymer, and reacting the isocyanate group-containing prepolymer with the above specific component C. Such a method makes it possible to prepare an amphoteric urethane resin simply and safely as compared with a conventional method. In the above preparation method, when both specific components C and D are simultaneously reacted, together with the components A and B, the carboxyl group(s) in the component C and the tertiary amino group(s) in the component D form(s) a salt, which is insoluble in the reaction system. As a result, the reaction with the isocyanate compound does not occur even in the presence of the OH group(s), thereby making it impossible to prepare a desired amphoteric urethane resin.

The above polyol compound (component A) is not specifically limited as far as it can be used in the preparation of a normal polyurethane, and examples thereof include polyester polyol, polyether polyol, polycarbonate polyol, polybutadiene polyol, polyisoprene



polyol, polyolefin polyol and polyacrylate polyol, etc. These polyol compounds are used alone or in combination. Among these polyol compounds, polyester polyol and polyether polyol are preferably used.

5        Examples of the polyester polyol include those obtained by polycondensing at least one of dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, sebacic acid, azelaic acid, maleic acid, fumaric acid, phthalic acid and terephthalic acid with at least one of  
10 polyhydric alcohols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 1,6-hexanediol, neopentyl glycol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, spiro-glycol and trimethylolpropane, etc., and those obtained by the ring-opening  
15 polymerization of lactones.

Example of the polyether polyol include polyhydric alcohols used in the synthesis of the said polyester polyols, phenols such as bisphenol A, or those obtained by the ring-opening addition polymerization of primary  
20 amines or secondary amines and cyclic ether such as ethylene oxide, propylene oxide, oxetane and tetrahydrofuran. Examples thereof include polyoxyethylene polyol, polyoxypropylene polyol, polyoxytetramethylene polyol, and those obtained by the  
25 ring-opening addition polymerization of bisphenol A and

at least one of propylene oxide and ethylene oxide, etc.  
(in case of a copolymer it may be either a block  
copolymer or a random copolymer).

The polyisocyanate compound (component B) is  
5 not specifically limited, and examples thereof include

organic diisocyanate compounds such as aliphatic  
diisocyanate compound, alicyclic diisocyanate compound  
and aromatic diisocyanate compound. These compounds  
may be used alone or in combination.

10 Example of the aliphatic diisocyanate compound  
includes ethylene diisocyanate, 2,2,4-trimethylhexa-  
methylene diisocyanate, 1,6-hexamethylene diisocyanate,  
etc. Examples of the alicyclic diisocyanate compound  
includes hydrogenated 4,4'-diphenylmethane  
15 diisocyanate, 1,4-cyclohexane diisocyanate,  
methylcyclohexylene diisocyanate, isophorone  
diisocyanate and norbornane diisocyanate, etc.  
Examples of the aromatic diisocyanate compound  
includes 4,4'-diphenylmethane diisocyanate, xylylene  
20 diisocyanate, toluene diisocyanate and naphthalene  
diisocyanate, etc. Among these compounds, 1,6-  
hexamethylene diisocyanate, isophorone diisocyanate,  
norbornane diisocyanate, etc. are preferable because of  
the excellent light resistance and low price.

25 The compound (component C) having active

hydrogen(s) and carboxyl group(s) is not specifically limited as far as it is a compound having at least one active hydrogen and at least one carboxyl group in a molecule, and examples thereof include  
5 dimethylolpropionic acid (DMPA), dimethylolbutanoic acid, carboxyl group-containing polycaprolactone diol, etc. These compounds may be used alone or in combination.

The compound (component D) having the above  
10 active hydrogen(s) and tertiary amino group(s) is not specifically limited as far as it is a compound having at least one active hydrogen and at least one tertiary amino group in a molecule, and examples thereof include N-alkyldialkanolamine compound such as N-  
15 methyldiethanolamine and N-butyldiethanolamine, and dimethylaminoethanol, etc. These compounds may be used alone or in combination.

In the production of an isocyanate group-containing prepolymer by using the above respective  
20 components, chain extenders or molecular weight inhibitors can be used for the purpose of controlling various characteristics of the amphoteric urethane resin as a final product.

The chain extender is not specifically limited and  
25 examples thereof include low-molecular polyol, amines,

etc. Examples of the low-molecular polyol includes glycols such as ethylene glycol, propylene glycol, 1,4-butanediol, diethylene glycol, 1,6-hexanediol, spiro-glycol, cyclohexyl dimethanol, hydrogenated bisphenol A,  
5 neopentyl glycol, bis(beta-hydroxyethoxy)benzene, and xylylene glycol; and triol such as trimethylolpropane and glycerin. Examples of the amines include ethylenediamine, propylenediamine, piperazine, hydrazine, isophoronediamine, methylene(bis-o-  
10 chloroaniline) and propylene glycol having amino groups at both ends, etc.

Examples of the molecular weight inhibitor includes propylene glycol having an amino group at one end, etc.

15 In the production of the amphoteric urethane resin, solvents can be used as needed. For example, organic solvents capable of dissolving both raw materials and polyurethane to be prepared are preferably used. Examples of the organic solvent includes amides such as  
20 N-methylpyrrolidone, dimethylformamide and dimethylacetamide; ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate; cellosolve acetate, cellosolve ether, etc..

In the production of the amphoteric urethane  
25 resin, the dispersibility in water can be provided by

neutralizing the carboxyl group(s) or tertiary amino group(s) incorporated into the molecule with a neutralizing agent. Examples of the neutralizing agent for the said carboxyl group(s) includes triethylamine,

5 trimethylamine, 2-amino-2-methyl-1-propanol,

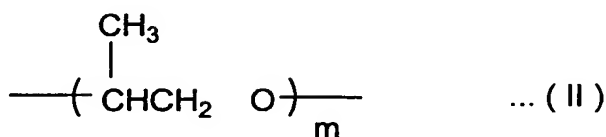
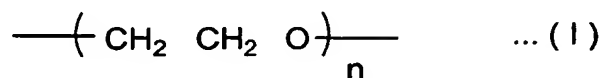
triethanolamine, potassium hydroxide, sodium hydroxide, etc. Examples of the neutralizing agent for the said tertiary amino group(s) include acetic acid, hydrochloric acid, sulfuric, nitric acid and dimethylsulfuric acid, etc.

10 In the production of the amphoteric urethane resin, polymerization catalysts known in the field of polyurethane can be used, and examples thereof include tertiary amine catalyst, organometallic catalyst, etc. Examples of the tertiary amine catalyst includes  
15 [2,2,2]diazabicyclooctane (DABCO), tetramethylene-amine, N-methyl morpholine and diazabicycloundecene (DBU), etc. Examples of the organometallic catalyst includes dibutyltin dilaurate, etc.

As the amphoteric urethane resin, in view of the  
20 hair washability, those having structural unit(s) derived from ethylene oxide (EO) in the structure are preferably used.

Examples of the structural unit derived from the said EO includes EO unit represented by the general  
25 formula (I) described below, propylene oxide (hereinafter

abbreviated to "PO") unit represented by the general formula (II) described below, etc., and the EO unit is preferably used.



- 5           The above amphoteric urethane resin may have both EO and PO units. A proportion of the EO unit to the PO unit is preferably within a range from 10/0 to 2/8, and particularly preferably from 10/0 to 4/6, on a weight basis.
- 10           The repeating number  $n$  of the EO unit in the general formula (I) is preferably set within a range from 3 to 300, and particularly preferably from 20 to 120. When the  $n$  is less than 3, sufficient hydrophilicity can not be
- 15   to be incorporated into the amphoteric urethane resin and, therefore, sufficient hair washability are not likely to be obtained. On the other hand, when  $n$  exceeds 300, an adverse influence is likely to be exerted on the moisture resistance or the like because of too strong hydrophilicity
- 20   of the amphoteric urethane resin. Furthermore, the repeating number  $m$  of the PO unit in the general formula

(II) is preferably set within a range from 3 to 300, and particularly preferably from 20 to 120. When the amphoteric urethane resin has both EO and PO units, (n + m) is preferably set within a range from 3 to 300, and particularly preferably from 20 to 120.

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The amphoteric urethane resin having structural unit(s) derived from ethylene oxide (EO) can be prepared, for example, by reacting a polyol compound (component A), a polyisocyanate compound (component B), a polyethylene oxide derivatives having active hydrogen(s), and a compound having active hydrogen(s) and carboxyl group(s) (component C) in the presence of excess isocyanate groups to form an isocyanate group-containing prepolymer, and reacting the isocyanate group-containing prepolymer with a compound having active hydrogen(s) and tertiary amino group(s) (component D). Alternatively, the amphoteric urethane resin can also be prepared by replacing the sequence of the reaction between the above components C and D. As the above components A to D, the same compounds as those described above can be used.

Examples of the polyethylene oxide derivative having active hydrogen(s) to be used together with the above components A to D is not specifically limited as far as it is capable of introducing a structural unit derived

from ethylene oxide (EO) into the structure of the above amphoteric urethane resin, and examples thereof include polyoxyethylene glycol (PEG), polyoxyethylene polyoxypropylene glycol (EOPO block copolymer), etc.

5 Among these, polyoxyethylene glycol is preferably used.

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The above polyoxyethylene oxide derivative may be any of a type wherein an OH group is introduced at both ends, a type wherein an NH<sub>2</sub> group is introduced at both ends, a type wherein an OH group is introduced at one  
10 end, and a type wherein an NH<sub>2</sub> group is introduced at one end. When using the type wherein an OH group is introduced at both ends or a type wherein an NH<sub>2</sub> group is introduced at both ends, an amphoteric urethane resin having the EO unit(s) in a principal chain is obtained.  
15 When using the type wherein an OH group is introduced at one end or a type wherein an NH<sub>2</sub> group is introduced at one end, an amphoteric urethane resin having EO unit(s) at its side chain(s) or end(s) is obtained.

The molecular weight of the specific polyethylene  
20 oxide derivative is preferably within a range from 200 to 20000, and particularly preferably from 1000 to 10000.

To further improve the feel, those having polysiloxane bond(s) in the structure are preferably used as the amphoteric urethane resin.

25 The repeating number n of a siloxane bond (Si-O)



is preferably within a range from 5 to 300, and particularly preferably from 20 to 150. When n is less than 5, it becomes difficult to obtain the sufficient effect on the touch, coming properties, etc. obtained  
5 intrinsically by introducing the polysiloxane bond(s)

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because of too small amount of the polysiloxane bond(s) in the resulting amphoteric urethane resin. On the other hand, when n exceeds 300, the compatibility with other raw materials become inferior because of high  
10 hydrophobicity, thereby making it difficult to react them. Furthermore, the adhesion to hair is likely to be inhibited because of too high hydrophobicity of the resulting polymer.

The amphoteric urethane resin having the said  
15 polysiloxane bond(s) can be prepared, for example, by reacting a polyol compound (component A), a polyisocyanate compound (component B), a polysiloxane compound having active hydrogen(s) and a compound having active hydrogen(s), and carboxyl group(s)  
20 (component C) in the presence of excess isocyanate groups to form an isocyanate group-containing prepolymer, and reacting the isocyanate group-containing prepolymer with a compound having active hydrogen(s) and tertiary amino group(s) (component D).  
25 Alternatively, the amphoteric urethane resin can also be

prepared by replacing the sequence of the reaction between the above components C and D. As the above components A to D, the same compounds as those described above can be used.

5       The polysiloxane compound having active hydrogen(s) to be used together with the above components A to D is not specifically limited as far as it is capable of introducing polysiloxane bond(s) into the structure of the amphoteric urethane resin, and examples  
10   thereof include polydialkylsiloxanediol, polydialkylsiloxanemonool, polydialkylsiloxanediamine, polydialkylsiloxanemonoamine, etc. These compounds may be used alone or in combination. The alkyl group(s) to be combined with Si of the respective siloxane bonds of the  
15   said polydialkylsiloxanediol preferably has 1 to 10 carbon atoms, and particularly preferably 1 to 5 carbon atoms. The above polysiloxane compound may contain various siloxane bonds wherein the number of carbon atoms of the alkyl group(s) to be combined with Si of the siloxane  
20   bonds varies. Specific examples of the polydialkylsiloxanediol include polydimethylsiloxanediol, polymethylethylsiloxanediol, etc. Examples of the polydialkylsiloxanemonool include polydimethylsiloxanemonool, polymethylethylsiloxanemonool, etc. Examples of the  
25   polydialkylsiloxanediamine include polydimethylsiloxane-

diamine, polymethylethyl-siloxanediamine, etc.  
Examples of the polydialkyl-siloxanemonoamine include  
poly-dimethylsiloxane-monoamine,  
polymethylethylsiloxane-monomaine, etc.

- 5        Examples of the polysiloxane compound include a  
type wherein an OH group is introduced at both ends, a  
type wherein an NH<sub>2</sub> group is introduced at both ends, a  
type wherein an OH group is introduced at one end and a  
type wherein an NH<sub>2</sub> group is introduced at one end.
- 10    When using the type wherein an OH group is introduced  
at both ends or a type wherein an NH<sub>2</sub> group is  
introduced at both ends, an amphoteric urethane resin  
having polysiloxane bond(s) in a principal chain is  
obtained. When using the type wherein an OH group is
- 15    introduced at one end or a type wherein an NH<sub>2</sub> group is  
introduced at one end, an amphoteric urethane resin  
having polysiloxane bond(s) at its side chain(s) or end(s)  
is obtained.

In the cosmetics of the present invention, the

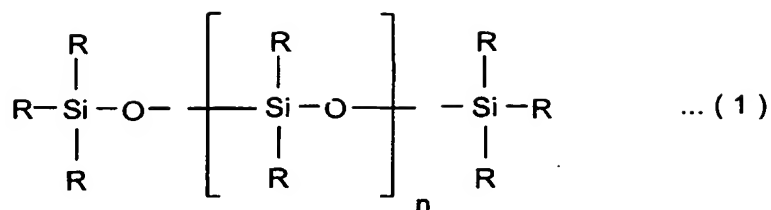
20    amphoteric urethane resin is preferably used in the form  
of an aqueous solution. In the present invention, the  
aqueous solution includes not only an aqueous solution  
state where the amphoteric urethane resin is completely  
dissolved in water but also a water dispersion state

where the amphoteric urethane resin is dispersed in water.

It is also possible to add a crosslinking agent such as silane coupling agent to the water dispersion of the  
5 above amphoteric resin, thereby to provide the crosslinkability. To provide the storage stability, various additives may be added and examples thereof include protective colloidal agents, bactericides, mildewproofing agents, etc.

10 The silicone polymer used together with the said amphoteric urethane resin is not specifically limited as far as it has polysiloxane bond(s) in a molecule and can be used in cosmetics, and examples thereof include silicone resin, silicone oil, silicone emulsion, silicone  
15 rubber, etc. Examples of the silicone rubber include nonionic, polyether-modified, phenyl-modified, amino-modified, alkyl-modified, alkoxy-modified, cyclic silicone polymers, etc. These silicone polymers can be used alone or in combination.

20 Examples of the nonionic silicone polymer includes those represented by the following general formula (1):

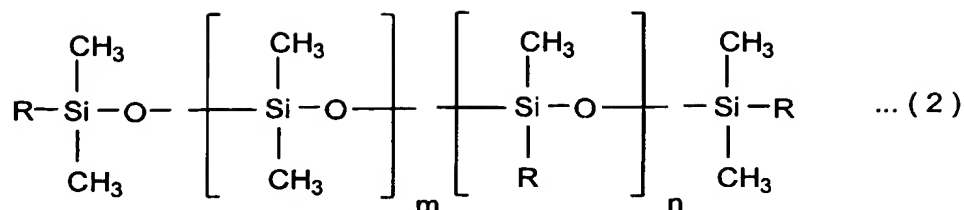


[wherein R represents a hydrogen atom, hydrocarbon group(s) having 1 to 12 carbon atoms, or  $-\text{OSi}(\text{CH}_3)_3$  and may be the same or different; and n represents a numeral  
5 of 3 or more].

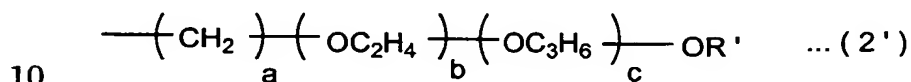
In the general formula (1), the hydrocarbon group(s) having 1 to 12 carbon atoms is/are straight-chain or branched-chain saturated hydrocarbon group(s) and is/are preferably methyl group(s), while n is  
10 preferably from 50 to 3000.

Examples of the nonionic silicone polymer represented by the general formula (1) include methyl polysiloxane whose R is entirely methyl group(s).

Examples of the polyether-modified silicone  
15 polymer includes those represented by the following general formula (2). Each repeating unit in the silicone polymer of the present invention may be in any form of polymerization such as random polymerization and block polymerization.



[wherein R represents hydrocarbon group(s) having 1 to 12 carbon atoms or group(s) represented by the following general formula (2') and may be the same or different, provided that at least one of R(s) is group(s) represented by the following general formula (2'); m represents 0 or a numeral of 1 or more; and n represents a numeral of 1 or more]

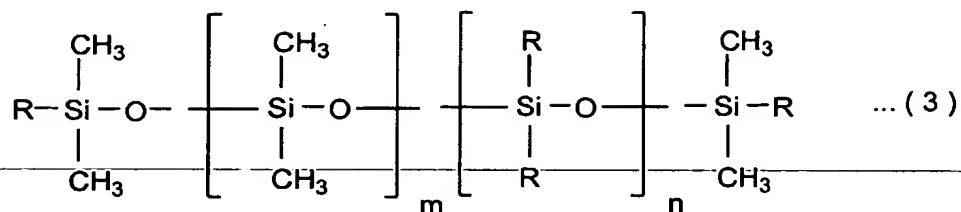


(wherein R' represents a hydrogen atom or hydrocarbon group(s) having 1 to 10 carbon atoms; a represents a numeral of 1 to 10; b represents a numeral of 1 to 300; and c represents a numeral of 0 to 300)

15. In the general formula (2), the hydrocarbon group(s) having 1 to 12 carbon atoms represented by R include(s) a straight-chain or branched-chain saturated hydrocarbon group(s). m is preferably from 10 to 500, and n is preferably from 1 to 500. In the general formula (2'), a is preferably 2 to 4, b is preferably from 2 to 50, and c is preferably from 0 to 5.

Examples of the phenyl-modified silicone polymer

includes those represented by the following general formula (3):

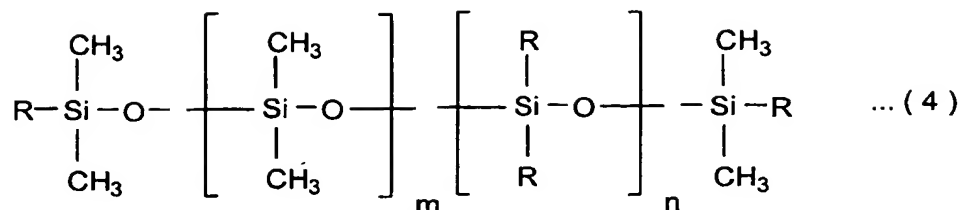


5 [wherein R represents hydrocarbon group(s) having 1 to 12 carbon atoms,  $-\text{OSi}(\text{CH}_3)_3$  or phenyl group(s) and may be the same or different, provided that at least one of R(s) is phenyl group(s); m represents 0 or a numeral of 1 or more; and n represents a numeral of 1 or more].

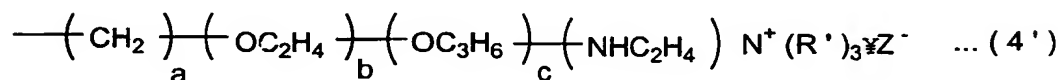
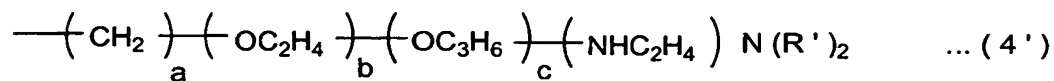
10 In the general formula (3), the hydrocarbon group(s) having 1 to 12 carbon atoms represented by R include(s) straight-chain or branched-chain saturated hydrocarbon group(s). m is preferably from 0 to 500, and n is preferably from 1 to 2000.

15 As the phenyl-modified silicone polymer represented by the general formula (3) methylphenyl polysiloxane is preferably used.

Examples of the amino-modified silicone polymer includes those represented by the following general  
20 formula (4):



[wherein R represents a hydrogen atom, hydrocarbon group(s) having 1 to 12 carbon atoms, hydroxyl group(s), methoxy group(s) or group(s) represented by the following general formula (4') or (4'') and may be the same or different, provided that at least one of R(s) is group(s) represented by the following general formula (4') or (4''); m represents 0 or a numeral of 1 or more; and n represents a numeral of 1 or more



(wherein R' represents a hydrogen atom or hydrocarbon group(s) having 1 to 6 carbon atoms and may be the same or different; Z represents a halogen ion or an organic anion; a represents a numeral of 1 to 6; b represents a numeral of 0 to 6; and c represents a numeral of 0 to 6)].

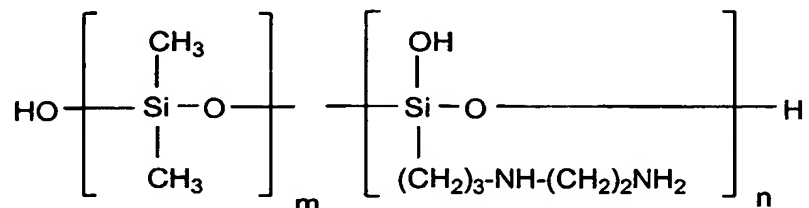
In the general formula (4), the hydrocarbon group(s) having 1 to 12 carbon atoms represented by R



include(s) straight-chain or branched-chain saturated hydrocarbon group(s). m is preferably from 3 to 500, and n is preferably from 1 to 500. In the general formulas (4') and (4''), the hydrocarbon group(s) having 1 to 6 carbon atoms represented by R' include(s) straight-chain

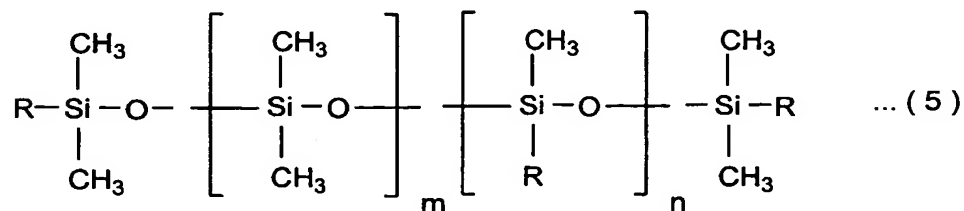
or branched-chain saturated hydrocarbon group(s).

As the amino-modified silicone polymer represented by the said general formula (4), aminodimethicone represented by the following structural formula is preferably used.



[wherein m and n are as defined in the general formula (4)]

Examples of the alkyl-modified silicone polymer include, those represented by the following general formula (5):

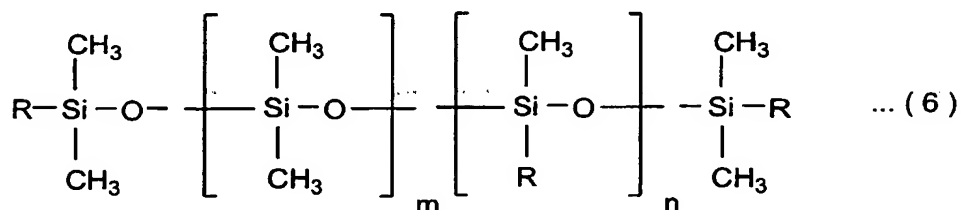


[wherein R represents hydrocarbon group(s) having 1 to

50 carbon atoms and may be the same or different, provided that at least one of R(s) is hydrocarbon group(s) having 12 to 50 carbon atoms; m represents 0 or a numeral of 1 or more; and n represents a numeral of 1 or more].

In the general formula (5), the hydrocarbon group(s) having 1 to 50 carbon atoms represented by R include(s) straight-chain or branched-chain saturated hydrocarbon group(s), and hydrocarbon group(s) having 12 to 50 carbon atoms is/are preferably used, and hydrocarbon group(s) having 15 to 40 carbon atoms is/are more preferably used. m is preferably from 10 to 500, and n is preferably from 10 to 500.

Examples of the alkoxy-modified silicone polymer include those represented by the following general formula (6):

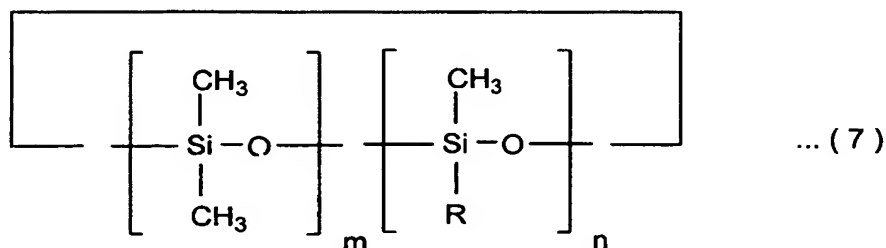


[wherein R represents hydrocarbon group(s) having 1 to 12 carbon atoms or alkoxy group(s) having 1 to 50 carbon atoms and may be the same or different, provided that at least one of R(s) is alkoxy group(s) having 1 to 50

carbon atoms; m represents 0 or a numeral of 1 or more; and n represents a numeral of 1 or more].

In the general formula (6), the hydrocarbon group(s) having 1 to 12 carbon atoms represented by R  
 5 include(s) straight-chain or branched-chain saturated hydrocarbon group(s). The alkoxy group(s) having 1 to 50 carbon atoms represented by R include(s) straight-chain or branched-chain saturated alkoxy group(s) and alkoxy group(s) having 1 to 20 carbon atoms is/are  
 10 preferably used. m is preferably from 3 to 500, and n is preferably from 1 to 100.

Examples of the cyclic silicone polymer includes those represented by the following general formula (7):



15 [wherein R represents hydrocarbon group(s) having 1 to 12 carbon atoms and may be the same or different in each repeating unit; m represents 0 or a numeral of 1 or more; n represents a numeral of 1 or more; and m + n is from 4 to 10].

20 In the general formula (7), the hydrocarbon group(s) having 1 to 12 carbon atoms represented by R

include(s) straight-chain or branched-chain saturated hydrocarbon group(s).

The average molecular weight of these silicone polymers is preferably within a range from 100 to 5 10,000,000, and particularly preferably from 10,000 to 1,000,000.

The silicone polymer is preferably used in the form of an aqueous solution or a water dispersion in view of the stability for cosmetics.

10 The incorporation ratio of the amphoteric urethane resin to the silicone polymer is preferably within a range from 0.1/100 to 100/0.01, and particularly preferably from 100/0.01 to 100/5, in terms of a weight ratio.

Furthermore, any components used commonly in 15 cosmetics such as pigments, coloring matters, colorants, perfumes, surfactants, humectants, preservatives, antiseptics, bactericides, antioxidants, oil agents, viscosity modifier and ultraviolet absorbers can be contained in the cosmetic of the present invention, in 20 addition to the amphoteric urethane resin and silicone polymer.

The cosmetics of the present invention can be prepared, for example, by the following methods.

Preparation of hair cosmetics (foam hair fixatives)

25 In the aqueous solution of the amphoteric

urethane resin thus obtained described above, a silicone polymer, various surfactants such as polyoxyethylene alkyl ether, and coconut oil fatty acid diethanolamide, ethanol, deionized water, etc. are  
5 blended in the predetermined proportion, and mixed until  
they are made homogenous to obtain a component X. Then, a component Y made of a propellant (LPG) is added to prepare a desired foam hair fixative.

Preparation of hair cosmetics (aerosol spray hair fixative)

10 In the aqueous solution of the above amphoteric urethane resin, a silicone polymer, deionized water, sodium dioctyl sulfosuccinate, ethanol, etc. are blended in the predetermined proportion, and mixed until they are made homogenous to obtain a component X. Then, a  
15 component Y made of a propellant (LPG) is added to prepare a desired aerosol spray hair fixative.

Preparation of hair cosmetics (gel-like hair fixatives)

First, a viscosity modifier, triethanolamine, ethanol, deionized water, etc. are blended in the  
20 predetermined proportion, and then mixed until a viscous gel is formed to obtain a component X. Then, a silicone polymer, ethanol, deionized water, etc. are blended in the aqueous solution of the amphoteric urethane resin in the predetermined proportion to obtain a component Y. The  
25 resulting component Y is added to the above component,

and mixed until they are made homogenous to prepare a desired gel-like hair fixative.

Preparation of hair cosmetics (pump spray hair fixatives)

In the aqueous solution of the amphoteric urethane resin, a silicone polymer, sodium dioctyl sulfosuccinate, ethanol, deionized water, etc. are blended in the predetermined proportion, and mixed until they are made homogenous to prepare a desired pump spray hair fixative.

10 Furthermore, skin care cosmetics such as shaving cream, skin care lotion and sunscreen lotion; and make-up cosmetics such as nail polish, mascara and foundation can be prepared according to the general preparation methods of these cosmetics.

15 Examples

The following Examples and Comparative Examples further illustrate the present invention in detail.

The following materials were prepared before describing the Examples and Comparative Examples.

20 Amphoteric urethane resin (a)

In a glass four-necked flask equipped with a stirrer, a thermometer, a nitrogen introducing tube and a reflux condenser, 100 g of isophorone diisocyanate (IPDI), 60 g of polypropylene glycol (PPG having a  
25 molecular weight of 1000), 5 g of cyclohexyl dimethanol

(CHDM), and 38 g of dimethylolbutanoic acid (DMBA) were charged, and then 60 g of ethyl acetate as a solvent was added and the mixture was heated to 80 degree C in an oil bath and allowed to react for four hours. Then, 2 g  
5 of N-methyldiethanolamine and 30 g of ethyl acetate were added furthermore, and the mixture was allowed to react for additional three hours. To the resulting mixture, 30 g of polypropylene glycol having an amino group at one end (Jeffamine M1000, manufactured by HUNTSMAN  
10 CORPORATION) and 50 g of ethyl acetate were added furthermore, and the mixture was allowed to react for additional one hour to obtain a solution of a polyurethane prepolymer having residual NCO groups. The polyurethane prepolymer having residual NCO groups  
15 was dispersed in 750 g of water containing 16 g of potassium hydroxide and then polymerized by the chain-extending reaction at 50 degree C for three hours. Ethyl acetate was recovered from the resulting water dispersion under reduced pressure to obtain an  
20 amphoteric urethane resin which did not substantially contain the solvent.

Amphoteric urethane resin (b)

In a glass four-necked flask equipped with a stirrer, a thermometer, a nitrogen introducing tube and a  
25 reflux condenser, 100 g of isophorone diisocyanate

(IPDI), 60 g of polypropylene glycol (PPG having a molecular weight of 1000), 5 g of cyclohexyl dimethanol (CHDM), 20 g of polyoxyethylene glycol (PEG having a molecular weight of 1000) and, 36 g of dimethylolbutanoic acid (DMBA) were charged, and then 5 60 g of ethyl acetate as a solvent was added, and the mixture was heated to 80 degree C in an oil bath and allowed to react for four hours. Then, 2 g of N-methyldiethanolamine and 30 g of ethyl acetate were 10 added furthermore, and the mixture was allowed to react for additional three hours. To the resulting mixture, 30 g of polypropylene glycol having an amino group at one end (Jeffamine M1000, manufactured by HUNTSMAN CORPORATION), and 50 g of ethyl acetate were added 15 furthermore, and the mixture was allowed to react for additional one hour to obtain a solution of a polyurethane prepolymer having residual NCO groups. The polyurethane prepolymer having residual NCO groups was dispersed in 750 g of water containing 15 g of 20 potassium hydroxide and then polymerized by the chain-extending reaction at 50 degree C for three hours. Ethyl acetate was recovered from the resulting water dispersion under reduced pressure to obtain an aqueous substance of an amphoteric urethane resin which did not



substantially contain the solvent and had ethylene oxide chain(s) in the structure.

Amphoteric urethane resin (c)

In a glass four-necked flask equipped with a stirrer, a thermometer, a nitrogen introducing tube and a reflux condenser, 100 g of isophorone diisocyanate (IPDI), and 3 g of polydimethylsiloxanediol having two OH groups at one end (molecular weight: 1000) were charged, and then the mixture was heated to 80 degree C in an oil bath and allowed to react for two hours. Then, 55 g of polypropylene glycol (PPG having a molecular weight of 1000), 10 g of hydrogenated bisphenol A, and 36 g of dimethylolbutanoic acid (DMBA) were added, and then 60 g of ethyl acetate as a solvent was added, and the mixture was heated to 80 degree C in an oil bath and allowed to react for four hours. Then, 2 g of N-methyldiethanolamine and 30 g of ethyl acetate were added furthermore, and the mixture was allowed to react for additional three hours. To the resulting mixture, 30 g of polypropylene glycol having an amino group at one end (Jeffamine M1000, manufactured by HUNTSMAN CORPORATION) and 50 g of ethyl acetate were added furthermore, and the mixture was allowed to react for additional one hour to obtain a solution of a polyurethane prepolymer having residual NCO groups. The

polyurethane prepolymer having residual NCO groups was dispersed in 750 g of water containing 15 g of potassium hydroxide and then polymerized by the chain-extending reaction at 50 degree C for three hours. Ethyl

5 acetate was recovered from the resulting water

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dispersion under reduced pressure to obtain an aqueous substance of an amphoteric urethane resin which did not substantially contain the solvent and had dimethylsiloxane chain(s) in the structure.

10 Silicone polymer (1) (nonionic)

Methylpolysiloxane (SH200C-2 manufactured by DOW CORNING TORAY SILICONE CO., LTD.)

Silicone polymer (2) (polyether-modified)

SH3771C manufactured by DOW CORNING  
15 TORAY SILICONE CO., LTD.

Silicone polymer (3) (phenyl-modified)

Methylphenylpolysiloxane (SH556 manufactured by DOW CORNING TORAY SILICONE CO., LTD.)

Silicone polymer (4) (amino-modified)

20 Amodimethicone (SM8702C manufactured by DOW CORNING TORAY SILICONE CO., LTD.)

Silicone polymer (5) (alkyl-modified)

KF-412 manufactured by SHIN-ETSU CHEMICAL CO., LTD.

Silicone polymer (6) (alkoxy-modified)

KF-851 manufactured by SHIN-ETSU CHEMICAL CO., LTD.

Silicone polymer (7) (cyclic)

5 SH245 manufactured by DOW CORNING TORAY

SILICONE CO., LTD.

Polyoxyethylene stearyl ether

NIKKOL BS-20 manufactured by NIKKO CHEMICALS CO., LTD.

10 Coconut oil fatty acid diethanolamide

Amicol CDE-1 manufactured by MIYOSHI OIL & FAT CO., LTD.

Sodium dioctyl sulfosuccinate

Monawet MO-70E manufactured by MONA  
15 INDUSTRIES INC.

Viscosity modifier

Alkyl acrylate-polyoxyethylene stearyl ether itaconate copolymer (Structure 2001 manufactured by National Starch and Chemical Company]

20 Hair cosmetics (foam hair fixatives)

Examples 1a to 21a, Comparative Examples 1a to 3a

The respective materials of a component X shown in Tables 1 to 4 described hereinafter were blended in the proportion shown in the same tables and mixed until  
25 they were made homogenous to obtain the component X.

Then, a component Y was added in the resulting component X in the proportion shown in the same tables to prepare a foam hair fixative, respectively. The proportion of the amphoteric urethane resin is  
5 represented by a dry weight (the same rule applies correspondingly to the following Examples and Comparative Examples).

Using the foam hair fixatives of the Examples and Comparative Examples thus obtained, the respective  
10 characteristics were evaluated according to the following criteria. The results are summarized in Tables 1 to 4 described hereinafter.

#### Feel

0.8 g of the foam hair fixative was applied to a  
15 strand of black virgin hairs (having a length of 25 cm and a weight of 5.0 g). Then, the strand of hairs after drying at room temperature was subjected to an organoleptic test using ten panelists and the feel for hair cosmetic was evaluated. Evaluation criteria are set as follows:

20 : The number of persons, who felt that the strand of hairs is very soft to the feel, is 9 or more.

: The number of persons, who felt that the strand of hairs is very soft to the feel, is within a range from 6 to 8.

: The number of persons, who felt that the strand of hairs is very soft to the feel, is within a range from 2 to 5.

×: The number of persons, who felt that the strand of hairs is very soft to the feel, is 1 or less.

### Spread

0.8 g of the foam hair fixative was applied to a strand of black virgin hairs (having a length of 25 cm and a weight of 5.0 g). Then, the strand was subjected to an organoleptic test using ten panelists and the spread for hair cosmetic was evaluated. Evaluation criteria are set as follows:

: The number of persons, who felt that the spread at the time of application is very good, is 9 or more.

: The number of persons, who felt that the spread at the time of application is very good, is within a range from 6 to 8.

: The number of persons, who felt that the spread at the time of application is very good, is within a range from 2 to 5.

×: The number of persons, who felt that the spread at the time of application is very good, is 1 or less.

### Touch

0.8 g of the foam hair fixative was applied on a strand of black virgin hairs (having a length of 25 cm and a weight of 5.0 g). Then, the strand of hairs after drying at room temperature was subjected to an organoleptic test using ten panelists and the touch for hair cosmetic was evaluated. Evaluation criteria are set as follows:

: The number of persons, who felt that the strand of hairs after drying is very smooth to the touch, is 9 or more.

: The number of persons, who felt that the strand of hairs after drying is very smooth to the touch, is within a range from 6 to 8.

: The number of persons, who felt that the strand of hairs after drying is very smooth to the touch, is within a range from 2 to 5.

×: The number of persons, who felt that the strand of hairs after drying is very smooth to the touch, is 1 or less.

### 20 Hair washability

0.6 g of the foam hair fixative was applied to black virgin hairs (having a length of 15 cm and a weight of 3 g), followed by drying to make a strand of hairs. After the strand of hairs was slightly loosen using hot water at

40 degree C, 0.4 g of a 10% shampoo solution was applied and the strand was washed for 30 seconds. After the strand was rinsed with hot water at 40 degree C to wash away the shampoo solution, and sufficiently dried at

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5 50 degree C, the hair washability for hair cosmetic were

evaluated. Evaluation criteria are set as follows:

- : The number of persons, who felt that the hair washability are very good because the strand after drying has not any setting ability, is 9 or more.
- 10 : The number of persons, who felt that the hair washability are very good because the strand after drying has not any setting ability, is within a range from 6 to 8.
- : The number of persons, who felt that the hair washability are very good because the strand after drying
- 15 has not any setting ability, is within a range from 2 to 5.
- ×: The number of persons, who felt that the hair washability are very good because the strand after drying has not any setting ability, is 1 or less.

Table 1

(Part)

(Foam hair Fixative)

		Examples						
		1a	2a	3a	4a	5a	6a	7a
Component X	Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	(Types)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
	Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Deionized water	77.2	77.2	77.2	77.2	77.2	77.2	77.2
Component Y	Polyoxyethylene stearyl ether	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	Coconut oil fatty acid diethanolamide	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Component Y	Propellant (LPG)	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Feel								
Spread								
Touch								
Hair washability								



Table 2  
(Foam Hair Fixative)  
(Part)

		Examples									
		8a	9a	10a	11a	12a	13a	14a			
Component X	Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
	(Types)	(b)	(b)	(b)	(b)	(b)	(b)	(b)			
	Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)			
	Deionized water	77.2	77.2	77.2	77.2	77.2	77.2	77.2			
	Polyoxyethylene stearyl ether	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0			
Component Y	Coconut oil fatty acid diethanolamide	0.8	0.8	0.8	0.8	0.8	0.8	0.8			
	Propellant (LPG)	8.0	8.0	8.0	8.0	8.0	8.0	8.0			
Feel											
Spread											
Touch											
Hair washability											

Table 3

(Foam Hair Fixative) (Part)

		Examples									
		15a	16a	17a	18a	19a	20a	21a			
Component X	Amphoteric urethane resin (Types)	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
	Silicone polymer (Types)	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	Deionized water	77.2	77.2	77.2	77.2	77.2	77.2	77.2			
	Polyoxyethylene stearyl ether	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0			
	Coconut oil fatty acid diethanolamide	0.8	0.8	0.8	0.8	0.8	0.8	0.8			
Component Y		8.0	8.0	8.0	8.0	8.0	8.0	8.0			
Propellant (LPG)		8.0	8.0	8.0	8.0	8.0	8.0	8.0			
Feel											
Spread											
Touch											
Hair washability											

Table 4  
(Foam Hair Fixative) (Product)

		Comparative Examples		
		1a	2a	3a
Component X	Amphoteric urethane resin (Types)	3.0 (a)	3.0 (b)	3.0 (c)
	Silicone polymer (Types)	-	-	-
	Deionized water	77.7	77.7	77.7
	Polyoxyethylene stearyl ether	0.5	0.5	0.5
	Ethanol	10.0	10.0	10.0
	Coconut oil fatty acid diethanolamide	0.8	0.8	0.8
	Component Y      Propellant (LPG)	8.0	8.0	8.0
Feel				
Spread				
Touch				
Hair washability				

As is apparent from the results shown in Tables 1 to 4, the foam hair fixatives of the Examples have very good feel and good spread at the time of application and are superior in touch and hair washability because the amphoteric urethane resin and silicone polymer are used in combination. It is also apparent that the foam hair fixatives of the Examples using the amphoteric urethane resin (b) having ethylene oxide chain(s) in its structure are markedly superior in hair washability. It is also apparent that the foam hair fixatives of the Examples using the amphoteric urethane resin (c) having polysiloxane bonds in its structure are markedly superior in touch.

To the contrary, the foam hair fixatives of the Comparative Examples have good feel because the amphoteric urethane resin is used, but are inferior in spread at the time of application.

Hair cosmetics (aerosol spray hair fixatives)

Examples 1b to 21b, Comparative Examples 1b to 3b

The respective materials of a component X shown in Tables 5 to 8 described hereinafter were blended in the proportion shown in the same tables and mixed until they are made homogenous to obtain the component X. Then, a component Y was added in the resulting

component X in the proportion shown in the same tables to prepare an aerosol spray hair fixative, respectively.

Using the aerosol spray hair fixatives of the Examples and Comparative Examples thus obtained, the  
5 respective characteristics were evaluated according to the criteria for hair cosmetics. The results are summarized in Tables 5 to 8 described hereinafter.

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Table 5  
(Aerosol spray hair fixative) (Parts)

	Examples						
	1b	2b	3b	4b	5b	6b	7b
Component X	Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0
	(Types)	(a)	(a)	(a)	(a)	(a)	(a)
	Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5
	(Types)	(1)	(2)	(3)	(4)	(5)	(7)
	Deionized water	7.0	7.0	7.0	7.0	7.0	7.0
	Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3
	Ethanol	49.2	49.2	49.2	49.2	49.2	49.2
Component Y		Propellant (LPG)		40.0	40.0	40.0	40.0
Feel							
Spread							
Touch							
Hair washability							

Table 6  
(Aerosol spray hair fixative) (Parts)

		Examples						
		8b	9b	10b	11b	12b	13b	14b
Component X	Amphoteric urethane resin (Types)	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Silicone polymer (Types)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Deionized water	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Ethanol	49.2	49.2	49.2	49.2	49.2	49.2	49.2
	Component Y	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Propellant (LPG)								
Feel								
Spread								
Touch								
Hair washability								

Table 7

(Aerosol spray hair fixative) (Parts)

		Examples									
		15b	16b	17b	18b	19b	20b	21b			
Component X	Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
	(Types)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
	Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)			
	Deionized water	7.0	7.0	7.0	7.0	7.0	7.0	7.0			
	Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3	0.3			
Ethanol		49.2	49.2	49.2	49.2	49.2	49.2	49.2			
Component Y	Propellant (LPG)	40.0	40.0	40.0	40.0	40.0	40.0	40.0			
Feel											
Spread											
Touch											
Hair washability											



Table 8  
(Aerosol spray hair fixative) (Parts)

		Comparative Examples		
		1b	2b	3b
Component X	Amphoteric urethane resin	3.0	3.0	3.0
	(Types)	(a)	(b)	(c)
	Silicone polymer	-	-	-
	(Types)	-	-	-
	Deionized water	7.0	7.0	7.0
	Sodium dioctyl sulfosuccinate	0.3	0.3	0.3
	Ethanol	49.7	49.7	49.7
Component Y	Propellant (LPG)	40.0	40.0	40.0
Feel				
Spread				
Touch				
Hair washability				

As is apparent from the results shown in Tables 5 to 8, the aerosol spray hair fixatives of the Examples have very good feel and good spread at the time of application and are superior in touch and hair washability because the amphoteric urethane resin and silicone polymer are used in combination. It is also apparent that the aerosol spray hair fixatives of the Examples using the amphoteric urethane resin (b) having ethylene oxide chain(s) in its structure are markedly superior in hair washability. It is also apparent that the aerosol spray hair fixatives of the Examples using the amphoteric urethane resin (c) having polysiloxane bond(s) in its structure are markedly superior in touch.

To the contrary, the aerosol spray hair fixatives of the Comparative Examples have good feel because the amphoteric urethane resin is used, but are inferior in spread at the time of application.

Hair cosmetics (jerry hair fixatives)

Examples 1c to 21c. Comparative Examples 1c to 3c

The respective materials of a component X shown in Tables 9 to 12 described hereinafter were blended in the proportion shown in the same tables and mixed until viscous gel is formed to obtain the component X. Then, a component Y which was prepared by blending the respective materials in the proportion shown in the same

table was added in the resulting component X and mixed until they are made homogenous to prepare a jelly hair fixative, respectively.

Using the jerry hair fixatives of the Examples and

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5 Comparative Examples thus obtained, the respective

characteristics were evaluated according to the criteria for hair cosmetics. The results are summarized in Tables 9 to 12 described hereinafter.

Table 9

(Parts)

(Gel-like hair fixative)

		Examples						
		1c	2c	3c	4c	5c	6c	7c
Component X	Thickener	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Triethanolamine	1.1	1.1	1.1	1.1	1.1	1.1	1.1
	Ethanol	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Deionized water	50.0	50.0	50.0	50.0	50.0	50.0	50.0
	Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Component Y	(Types)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
	Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Ethanol	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Deionized water	33.9	33.9	33.9	33.9	33.9	33.9	33.9
Feel								
Spread								
Touch								
Hair washability								



Table 11

(Gel-like hair fixative) (Parts)

	Examples									
	15c	16c	17c	18c	19c	20c	21c			
Component X	Thickener	1.5	1.5	1.5	1.5	1.5	1.5			
	Triethanolamine	1.1	1.1	1.1	1.1	1.1	1.1			
	Ethanol	5.0	5.0	5.0	5.0	5.0	5.0			
	Deionized water	50.0	50.0	50.0	50.0	50.0	50.0			
	Amphoteric urethane resin (Types)	3.0 (c)	3.0 (c)	3.0 (c)	3.0 (c)	3.0 (c)	3.0 (c)			
Component Y	Silicone polymer (Types)	0.5 (1)	0.5 (2)	0.5 (3)	0.5 (4)	0.5 (5)	0.5 (6)			
	Ethanol	5.0	5.0	5.0	5.0	5.0	5.0			
	Deionized water	33.9	33.9	33.9	33.9	33.9	33.9			
	Feel									
	Spread									
	Touch									
	Hair washability									

Table 12  
(Gel-like hair fixative) (Parts)

	Comparative Examples		
	1c	2c	3c
Component X	Thickener	1.5	1.5
	Triethanolamine	1.1	1.1
	Ethanol	5.0	5.0
	Deionized water	50.0	50.0
Component Y	Amphoteric urethane resin (Types)	3.0 (a)	3.0 (c)
	Silicone polymer	-	-
	(Types)	-	-
	Ethanol	5.0	5.0
	Deionized water	34.4	34.4
Feel			
Spread			
Touch			
Hair washability			

As is apparent from the results shown in Tables 9 to 12, the jelly hair fixatives of the Examples have very good feel and good spread at the time of application and are superior in touch and hair washability because the

5 amphoteric urethane resin and silicone polymer are used in combination. It is also apparent that the gel-like hair fixatives of the Examples using the amphoteric urethane resin (b) having ethylene oxide chain(s) in its structure are markedly superior in hair washability. It is also

10 apparent that the gel-like hair fixatives of the Examples using the amphoteric urethane resin (c) having polysiloxane bond(s) in its structure are markedly superior in touch.

To the contrary, the gel-like hair fixatives of the

15 Comparative Examples have good feel because the amphoteric urethane resin is used, but are inferior in spread at the time of application.

Hair cosmetics (pump spray hair fixatives)

Examples 1d to 21d, Comparative Examples 1d to 3d

20 The respective materials shown in Tables 13 to 16 described hereinafter were blended in the proportion shown in the same table and mixed until they are made homogenous to prepare a pump spray hair fixative, respectively.



Using the pump spray hair fixatives of the Examples and Comparative Examples thus obtained, the respective characteristics were evaluated according to the criteria for hair cosmetics. The results are

5 summarized in Tables 13 to 16 described hereinafter.

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Table 13

(Parts)

(Pump spray hair fixative)

	Examples						
	1d	2d	3d	4d	5d	6d	7d
Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0
(Types)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Deionized water	86.2	86.2	86.2	86.2	86.2	86.2	86.2
Feel							
Spread							
Touch							
Hair washability							

Table 14  
(Pump spray hair fixative)  
(Parts)

	Examples									
	8d	9d	10d	11d	12d	13d	14d			
Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
(Types)	(b)	(b)	(b)	(b)	(b)	(b)	(b)			
Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)			
Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3	0.3			
Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0			
Deionized water	86.2	86.2	86.2	86.2	86.2	86.2	86.2			
Feel										
Spread										
Touch										
Hair washability										

Table 15  
(Pump spray hair fixative) (Parts)

	Examples									
	15d	16d	17d	18d	19d	20d	21d			
Amphoteric urethane resin	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
(Types)	(c)	(c)	(c)	(c)	(c)	(c)	(c)			
Silicone polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
(Types)	(1)	(2)	(3)	(4)	(5)	(6)	(7)			
Sodium dioctyl sulfosuccinate	0.3	0.3	0.3	0.3	0.3	0.3	0.3			
Ethanol	10.0	10.0	10.0	10.0	10.0	10.0	10.0			
Deionized water	86.2	86.2	86.2	86.2	86.2	86.2	86.2			
Feel										
Spread										
Touch										
Hair washability										

Table 16  
(Pump spray hair fixative) (Parts)

	Comparative Examples		
	1d	2d	3d
Amphoteric urethane resin	3.0	3.0	3.0
(Types)	(a)	(b)	(c)
Silicone polymer	-	-	-
(Types)	-	-	-
Sodium dioctyl sulfosuccinate	0.3	0.3	0.3
Ethanol	10.0	10.0	10.0
Deionized water	86.7	86.7	86.7
Feel			
Spread			
Touch			
Hair washability			

As is apparent from the results shown in Tables 13 to 16, the pump spray hair fixatives of the Examples have very good feel and good spread at the time of application and are superior in touch and hair washability because the amphoteric urethane resin and silicone polymer are used in combination. It is also apparent that the pump spray hair fixatives of the Examples using the amphoteric urethane resin (b) having ethylene oxide chain(s) in its structure are markedly superior in hair washability. It is also apparent that the pump spray hair fixatives of the Examples using the amphoteric urethane resin (c) having polysiloxane bond(s) in its structure are markedly superior in feel.

To the contrary, the pump spray hair fixatives of the Comparative Examples have good feel because the amphoteric urethane resin is used, but are inferior in spread at the time of application.

Skin care cosmetics (skin care lotions)

Examples 1e to 7e. Comparative Example 1e

The respective materials of a component X shown in Tables 17 and 18 described hereinafter were blended in the proportion shown in the same tables and heated to 80 degree C to obtain the component X. The respective materials of a component Y were blended in the proportion shown in the same tables and heated to 80

degree C to obtain the component Y. Then, the component X and component Y were mixed, followed by stirring at 80 degree C for 30 minutes. A viscosity modifier was added, and mixed until they were made  
5 homogenous, then cooled down to 40 degree C to prepare a skin care lotion, respectively.

Using the skin care lotions of the Examples and Comparative Example thus obtained, the respective characteristics were evaluated according to the following  
10 criteria. The results are summarized in Tables 17 and 18 described hereinafter.

#### Feel

The feel for skin care cosmetic was evaluated at a practical use test using ten panelists. Evaluation criteria  
15 are set as follows:

: The number of persons, who did not feel tight and also felt soft, is 9 or more.

: The number of persons, who did not feel tight and also felt soft, is within a range from 6 to 8.

20 : The number of persons, who did not feel tight and also felt soft, is within a range from 2 to 5.

×: The number of persons, who did not feel tight and also felt soft, is 1 or less.

Spread

The spread for skin care cosmetic was evaluated by a practical use test using ten panelists. Evaluation criteria are set as follows:

5 : The number of persons, who felt that the spread at the time of application is very good, is 9 or more.

10 : The number of persons, who felt that the spread at the time of application is very good, is within a range from 6 to 8.

: The number of persons, who felt that the spread at the time of application is very good, is within a range from 2 to 5.

15 x: The number of persons, who felt that the spread at the time of application is very good, is 1 or less.



Table 17  
(Skin care lotion) (Parts)

	Examples	1e	2e	3e	4e
Component X	Octyl methoxycinnamate	7.5	7.5	7.5	7.5
	Ether polyoxystearate	1.0	1.0	1.0	1.0
	Emulsion type glyceryl stearate	1.0	1.0	1.0	1.0
	Stearic acid	1.5	1.5	1.5	1.5
	Mixture of titanium dioxide and C <sub>12-18</sub> alkyl benzoate	1.7	1.7	1.7	1.7
	Polyoxyethylene-added dimethicone	0.5	0.5	0.5	0.5
	Amphoteric urethane resin (a)	1.0	1.0	1.0	1.0
	Silicone polymer	0.3	0.3	0.3	0.3
	(Types)	(1)	(2)	(3)	(4)
	Deionized water	61.5	61.5	61.5	61.5
Component Y	Triethanolamine (99%)	4.0	4.0	4.0	4.0
	Antiseptic	q.s.	q.s.	q.s.	q.s.
	Thickener (2%)	20.0	20.0	20.0	20.0
	Feel				
Spread					

Table 18  
(Skin care lotion)  
(Parts)

	Examples	Comparative Example			
			5e	6e	7e
Component X	Octyl methoxycinnamate	7.5	7.5	7.5	7.5
	Ether polyoxystearate	1.0	1.0	1.0	1.0
	Emulsion type glyceryl stearate	1.0	1.0	1.0	1.0
	Stearic acid	1.5	1.5	1.5	1.5
	Mixture of titanium dioxide and C <sub>12-15</sub> alkyl benzoate	1.7	1.7	1.7	1.7
Component Y	Polyoxyethylene-added dimethicone	0.5	0.5	0.5	0.5
	Amphoteric urethane resin (a)	1.0	1.0	1.0	1.0
	Silicone polymer	0.3	0.3	0.3	—
	(Types)	(5)	(6)	(7)	—
	Deionized water	61.5	61.5	61.5	61.8
Feel	Triethanolamine (99%)	4.0	4.0	4.0	4.0
	Antiseptic	q.s.	q.s.	q.s.	q.s.
	Thickener (2%)	20.0	20.0	20.0	20.0
Spread					

As is apparent from the results shown in Tables 17 and 18, the skin care lotions of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are used in combination.

---

To the contrary, the skin care lotion of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 Skin care cosmetics (shaving creams)

Examples 1f to 7f. Comparative Example 1f

The respective materials of a component X shown in Tables 19 and 20 described hereinafter were blended in the proportion shown in the same tables and heated to 80 degree C to obtain the component X. The respective materials of a component Y were blended in the proportion shown in the same tables and heated to 80 degree C to obtain the component Y. Then, the component X and component Y were mixed at 80 degree C and cooled down to 40 degree C. An antiseptic and a perfume were added in a sufficient quantity to prepare shaving cream, respectively.

Using the shaving creams of the Examples and Comparative Example thus obtained, the respective characteristics were evaluated according to the criteria

for skin care cosmetics. The results are summarized in  
Tables 19 and 20 described hereinafter.

---

Table 19  
(Shaving cream) (Parts)

	Examples			
	1f	2f	3f	4f
Component X	Stearic acid	8.0	8.0	8.0
	Mineral oil	2.0	2.0	2.0
	Isopropyl myristate	2.0	2.0	2.0
	Glyceryl stearate	0.5	0.5	0.5
Component Y	Amphoteric urethane resin (a)	0.5	0.5	0.5
	Silicone polymer	0.3	0.3	0.3
	(Types)	(1)	(2)	(3)
	Deionized water	72.5	72.5	72.5
	Thickeners (2%)	10.0	10.0	10.0
Feel	Triethanolamine (99%)	4.2	4.2	4.2
Spread				

Table 20

(Parts)

(Shaving cream)

	Examples			Comparative Example
	5f	6f	7f	
Component X	8.0	8.0	8.0	8.0
	2.0	2.0	2.0	2.0
	2.0	2.0	2.0	2.0
	0.5	0.5	0.5	0.5
	0.5	0.5	0.5	0.5
Component Y	0.3	0.3	0.3	-
	(5)	(6)	(7)	-
	72.5	72.5	72.5	72.8
	10.0	10.0	10.0	10.0
	4.2	4.2	4.2	4.2
Feel				
Spread				

As is apparent from the results shown in Tables 19 and 20, the shaving creams of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are used in combination.

---

To the contrary, the shaving cream of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 Skin care cosmetics (sunscreen lotions)

Examples 1g to 7g. Comparative Example 1g

The respective materials of a component X shown in Tables 21 and 22 described hereinafter were blended in the proportion shown in the same tables and heated to 80 degree C to obtain the component X. The respective materials of a component Y were blended in the proportion shown in the same tables and heated to 80 degree C to obtain the component Y. Then, the component X and component Y were mixed at 80 degree C to prepare a sunscreen lotion, respectively.

Using the sunscreen lotions of the Examples and Comparative Example thus obtained, the respective characteristics were evaluated according to the criteria for skin care cosmetics. The results are summarized in Tables 21 and 22 described hereinafter.

Table 21  
(Sunscreen lotion) (Parts)

	Examples			
	1g	2g	3g	4g
Component X	Octyl cinnamate	7.50	7.50	7.50
	Octyl palmitate	5.00	5.00	5.00
	Cetyl alcohol	1.00	1.00	1.00
	Polyethylene glycol monostearate	1.50	1.50	1.50
	Poly(oxyethylene oxypropylene) methyl-polysiloxane copolymer	1.00	1.00	1.00
	Dimethylstearylamine	2.00	2.00	2.00
Component Y	Amphoteric urethane resin (a)	1.00	1.00	1.00
	Silicone polymer	0.50	0.50	0.50
	(Types)	(1)	(2)	(3)
	Purified water	69.5	69.5	69.5
		5	5	5
	Triethanolamine (99%)	0.70	0.70	0.70
	Thickeners (2%)	10.0	10.0	10.0
		0	0	0
	Antiseptic	0.25	0.25	0.25
	Feel			
	Spread			



Table 22  
(Sunscreen lotion) (Parts)

	Examples			Comparative Example
	5g	6g	7g	
Component X	Octyl cinnamate	7.50	7.50	7.50
	Octyl palmitate	5.00	5.00	5.00
	Cetyl alcohol	1.00	1.00	1.00
	Polyethylene glycol monostearate	1.50	1.50	1.50
	Poly(oxyethylene oxypropylene) methyl-polysiloxane copolymer	1.00	1.00	1.00
	Dimethylstearylamine	2.00	2.00	2.00
Component Y	Amphoteric urethane resin (a)	1.00	1.00	1.00
	Silicone polymer	0.50	0.50	0.50
	(Types)	(5)	(6)	(7)
	Purified water	69.5	69.5	69.5
		5	5	5
	Triethanolamine (99%)	0.70	0.70	0.70
	Thickeners (2%)	10.0	10.0	10.0
		0	0	0
	Antiseptic	0.25	0.25	0.25
	Feel			
	Spread			

As is apparent from the results shown in Tables 21 and 22, the sunscreen lotions of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are used in combination.

To the contrary, the sunscreen lotion of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 Make-up cosmetics (nail polishes)

Examples 1h to 7h, Comparative Example 1h

As shown in Tables 23 and 24 described hereinafter, a pigment was dispersed in deionized water in the proportion shown in the same tables and other  
15 components were added in the proportion shown in the same tables. The resultant was mixed until it was made homogenous with stirring and deaerated to prepare a nail polish, respectively.

Using the nail polishes of the Examples and  
20 Comparative Example thus obtained, the respective characteristics were evaluated according to the following criteria. The results are summarized in Tables 23 and 24 described hereinafter.

Feel

The feel for skin care cosmetic was evaluated at a practical use test using ten panelists. Evaluation criteria are set as follows:

5 : The number of persons, who did not feel tight and also felt soft, is 9 or more.

: The number of persons, who did not feel tight and also felt soft, is within a range from 6 to 8.

10 : The number of persons, who did not feel tight and also felt soft, is within a range from 2 to 5.

×: The number of persons, who did not feel tight and also felt soft, is 1 or less.

Spread

15 The spread for skin care cosmetic was evaluated at a practical use test using ten panelists. Evaluation criteria are set as follows:

: The number of persons, who felt that the spread at the time of application is very good, is 9 or more.

20 : The number of persons, who felt that the spread at the time of application is very good, is within a range from 6 to 8.

: The number of persons, who felt that the spread at the time of application is very good, is within a range from 2 to 5.

×: The number of persons, who felt that the spread at the time of application is very good, is 1 or less.

Table 23  
(Nail Polish) (Parts)

	Examples			
	1h	2h	3h	4h
Amphoteric urethane resin (a)	10.0	10.0	10.0	10.0
Silicone polymer	0.5	0.5	0.5	0.5
(Types)	(1)	(2)	(3)	(4)
Deionized water	86.1	86.1	86.1	86.1
Bentonite	0.6	0.6	0.6	0.6
Pigment	2.5	2.5	2.5	2.5
Perfume	0.1	0.1	0.1	0.1
Antiseptic	0.1	0.1	0.1	0.1
Silicone defoamer	0.1	0.1	0.1	0.1
Feel				
Spread				

Table 24  
(Nail polish)  
(Parts)

	Examples				Comparative Example
	5h	6h	7h	1h	
Amphoterie urethane resin (a)	10.0	10.0	10.0	10.0	10.0
Silicone polymer	0.5	0.5	0.5	-	-
(Types)	(5)	(6)	(7)	-	-
Deionized water	86.1	86.1	86.1	86.1	86.1
Bentonite	0.6	0.6	0.6	0.6	0.6
Pigment	2.5	2.5	2.5	2.5	2.5
Perfume	0.1	0.1	0.1	0.1	0.1
Antiseptic	0.1	0.1	0.1	0.1	0.1
Silicone defoamer	0.1	0.1	0.1	0.1	0.1
Feel					
Spread					

As is apparent from the results shown in Tables 23 to 24, the nail polishes of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are used in combination.

To the contrary, the nail polish of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 Make-up cosmetics (mascaras)

Examples 1i to 7i, Comparative Example 1i

As shown in Tables 25 and 26 described hereinafter, propylene glycol, triethanolamine, a viscosity modifier, and an antiseptic were blended with purified water in the proportion shown in the same tables and, after dissolving them at 80 degree C, the pigment was dispersed therein to form a water phase. Then, the respective materials of a component Z were blended in the proportion shown in the same tables and dissolved at 80 degree C to form an oil phase. The oil phase was added to the water phase and the mixture was emulsified by using a homogenizing mixer. Then, the respective materials of a component Y were gradually charged in the proportion shown in the same tables, followed by stirring

using a homogenizing mixer and further cooled down to room temperature to prepare a mascara, respectively.

Using the mascaras of the Examples and Comparative Example thus obtained, the respective

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5 characteristics were evaluated according to the criteria

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for make-up cosmetics. The results are summarized in Tables 25 and 26 described hereinafter.



Table 25  
(Mascara) (Parts)

	Examples			
	1i	2i	3i	4i
Component X	Propylene glycol	5.0	5.0	5.0
	Triethanolamine	1.0	1.0	1.0
	Thickener (2%)	10.0	10.0	10.0
	Antiseptic	0.5	0.5	0.5
	Pigment	10.0	10.0	10.0
Component Y	Purified water	51.0	51.0	51.0
	Amphoteric urethane resin (a)	10.0	10.0	10.0
	Silicone polymer	0.5	0.5	0.5
	(Types)	(1)	(2)	(3)
				(4)
Component Z	Stearic acid	6.0	6.0	6.0
	Beeswax	6.0	6.0	6.0
Feel				
Spread				

Table 26

(Mascara) (Parts)

		Examples			Comparative Example
		5i	6i	7i	
Component X	Propylene glycol	5.0	5.0	5.0	5.0
	Triethanolamine	1.0	1.0	1.0	1.0
	Thickener (2%)	10.0	10.0	10.0	10.0
	Antiseptic	0.5	0.5	0.5	0.5
	Pigment	10.0	10.0	10.0	10.0
	Purified water	51.0	51.0	51.0	51.0
	Amphoteric urethane resin (a)	10.0	10.0	10.0	10.0
Component Y	Silicone polymer	0.5	0.5	0.5	-
	(Types)	(5)	(6)	(7)	-
Component Z	Stearic acid	6.0	6.0	6.0	6.0
	Beeswax	6.0	6.0	6.0	6.0
Feel					
Spread					

As is apparent from the results shown in Tables 25 and 26, the mascaras of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are  
5 used in combination.

To the contrary, the mascara of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 Make-up cosmetics (foundations)

Examples 1j to 7j. Comparative Examples 1j

(i) Preparation of pigment

The respective components shown in Tables 27 and 28 described hereinafter were mixed in the  
15 proportion shown in the same tables and then pulverized through a pulverizer to prepare a pigment.

(ii) Preparation of water phase

Deionized water was heated to 70 degree C and bentonite was added to make swollen. Then, sodium  
20 carboxymethylcellulose dispersed previously in propylene glycol was dissolved by adding to the resulting solution. Triethanolamine, methylparaoxybenozate, and one selected from amphoteric urethane resin or a silicone polymer were added and dissolved thereto to prepare a  
25 water phase.

(iii) Preparation of oil phase

The respective components shown in Tables 27 and 28 described hereinafter were mixed in the proportion shown in the same tables and then dissolved

5 with heating to prepare an oil phase.

(iv) Preparation of pigment dispersion

A pigment dispersion was prepared by adding the above pigment to the water phase with stirring, followed by passing through a colloid mill.

10 (v) Emulsification

The above pigment dispersion and oil phase were heated to 75 degree C and 80 degree C, respectively, and the above oil phase was added to the pigment dispersion with stirring. After cooling the dispersion, a  
15 perfume was added at 45 degree C, and the stirring was continued up to the room temperature to prepare a foundation, respectively.

Using the foundations of the Examples and Comparative Example thus obtained, the respective  
20 characteristics were evaluated according to the criteria for make-up cosmetics. The results are summarized in Tables 27 and 28 described hereinafter.

Table 27

(Foundation) (Parts)

	Examples			
	1j	2j	3j	4j
Oil phase	Stearic acid	2.4	2.4	2.4
	Propylene glycol monostearate	2.0	2.0	2.0
	Cetostearyl alcohol	0.2	0.2	0.2
	Liquid lanolin	2.0	2.0	2.0
	Liquid paraffin	3.0	3.0	3.0
	Isopropyl myristate	8.5	8.5	8.5
	Propyl paraoxybenzoate	q.s.	q.s.	q.s.
Water phase	Amphoteric urethane resin (a)	0.5	0.5	0.5
	Silicone polymer	0.3	0.3	0.3
	(Types)	(1)	(2)	(3)
	Deionized water	63.3	63.3	63.3
	Sodium carboxymethylcellulose	0.2	0.2	0.2
	Bentonite	0.5	0.5	0.5
	Propylene glycol	4.0	4.0	4.0
Pigment	Triethanolamine	1.1	1.1	1.1
	Methyl paraoxybenzoate	q.s.	q.s.	q.s.
	Titanium oxide	8.0	8.0	8.0
	Talc	4.0	4.0	4.0
	Coloring pigment	q.s.	q.s.	q.s.
	Perfume	q.s.	q.s.	q.s.
	Feel			
Spread				

Table 28

(Foundation) (Parts)

		Examples			Comparative Example
		5j	6j	7j	
Oil phase	Stearic acid	2.4	2.4	2.4	1j
	Propylene glycol monostearate	2.0	2.0	2.0	2.0
	Cetostearyl alcohol	0.2	0.2	0.2	0.2
	Liquid lanolin	2.0	2.0	2.0	2.0
	Liquid paraffin	3.0	3.0	3.0	3.0
	Isopropyl myristate	8.5	8.5	8.5	8.5
	Propyl paraoxybenzoate	q.s.	q.s.	q.s.	q.s.
	Amphoteric urethane resin (a)	0.5	0.5	0.5	0.5
	Silicone polymer	0.3	0.3	0.3	-
Water phase	(Types)	(5)	(6)	(7)	-
	Deionized water	63.3	63.3	63.3	63.6
	Sodium carboxymethylcellulose	0.2	0.2	0.2	0.2
	Bentonite	0.5	0.5	0.5	0.5
	Propylene glycol	4.0	4.0	4.0	4.0
	Triethanolamine	1.1	1.1	1.1	1.1
	Methyl paraoxybenzoate	q.s.	q.s.	q.s.	q.s.
	Titanium oxide	8.0	8.0	8.0	8.0
	Talc	4.0	4.0	4.0	4.0
Pigment	Coloring pigment	q.s.	q.s.	q.s.	q.s.
	Perfume	q.s.	q.s.	q.s.	q.s.
Feel					
Spread					

As is apparent from the results shown in Tables 27 and 28, the foundations of the Examples have very good feel and good spread at the time of application because the amphoteric urethane resin and silicone polymer are used in combination.

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To the contrary, the foundation of the Comparative Example has good feel because the amphoteric urethane resin is used, but is inferior in spread at the time of application.

10 As described above, according to the cosmetics of the present invention, the amphoteric urethane resin and silicone polymer cause micro phase separation and the silicone polymer is unevenly distributed on the surface, thereby making it possible to provide the surface with the  
15 smoothness. As a result, the cosmetics are superior in spread at the time of application without impairing the touch when using the amphoteric urethane resin. The cosmetics of the present invention exhibit the excellent water resistance to neutral water as a result of ion  
20 bond(s) between the carboxyl group(s) and the tertiary amino group(s), while they exhibit excellent cleansing properties to shampoo as a result of the debonding of ions. Furthermore, the cationic tertiary amino group in the amphoteric urethane resin interacts with the surface  
25 of negatively charged hairs to exhibit good adhesion.

When using an aqueous solution or a water dispersion of a silicone polymer as the silicone polymer, the compatibility with the amphoteric urethane resin is enhanced to some degree, thereby making it possible to

5 ~~prepare a cosmetic having good stability.~~

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When structural units derived from ethylene oxide, as a nonionic hydrophilic component, is introduced into the structure of the amphoteric urethane resin, sufficient hydrophilicity is obtained and the hair washability are

10 particularly improved when using as the hair cosmetic.

When a polysiloxane bond(s) is/are introduced into the structure of the above amphoteric urethane resin, the touch is particularly improved furthermore when using as the hair cosmetic.



What is claimed is:

1. A cosmetic comprising an amphoteric urethane resin having carboxyl group(s) and tertiary amino group(s) in a molecule, and silicone polymer.

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2. The cosmetic according to claim 1, wherein said silicone polymer is a nonionic silicone polymer.

10        3. The cosmetic according to claim 1, wherein said silicone polymer is a polyether-modified silicone polymer.

15        4. The cosmetic according to claim 1, wherein said silicone polymer is a phenyl-modified silicone polymer.

20        5. The cosmetic according to claim 1, wherein said silicone polymer is an amino-modified silicone polymer.

25        6. The cosmetic according to claim 1, wherein said silicone polymer is an alkyl-modified silicone polymer.

7. The cosmetic according to claim 1, wherein said silicone polymer is an alkoxy-modified silicone polymer.

5 ——— 8. The cosmetic according to claim 1, wherein  
said silicone polymer is a cyclic silicone polymer.

9. The cosmetic according to any one of claims 1  
to 8, wherein said silicone polymer is in the form of an  
10 aqueous solution or a water dispersion.

10. The cosmetic according to any one of claims 1  
to 9, wherein said amphoteric urethane resin has  
structural unit(s) derived from ethylene oxide in its  
15 structure.

11. The cosmetic according to any one of claims 1  
to 9; wherein said amphoteric urethane resin has  
polysiloxane bond(s) in its structure.

20

12. The cosmetic according to any one of claims 1  
to 11, wherein said amphoteric urethane resin is in the  
form of an aqueous solution.

25

13. The cosmetic according to any one of claims 1 to 12, which is at least one selected from the group consisting of hair cosmetics, skin care cosmetics and make-up cosmetics.

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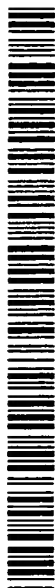
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(54) Title: COSMETIC COMPOSITIONS CONTAINING AMPHOTERIC URETHANE RISINS AND SILICONE POLYMERS

(57) Abstract: The present invention provides a cosmetic which is superior in both characteristics of feel and spread at the time of application. The cosmetic is a cosmetic comprising an amphoteric urethane resin having carboxyl group(s) and tertiary amino group(s) in a molecule, and a silicone polymer.

## INTERNATIONAL SEARCH REPORT

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According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
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<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 39688 A (TSUZUKI TOSHITAKA ;ASAOKA SEIJI (JP); KOYAMA KATSUYA (JP); SAKURAI) 12 August 1999 (1999-08-12) page 1, line 2-5, 25-28 page 2, line 1-5, 15-27 page 3, line 3-5, 9-15 page 6, line 19-22 page 7, line 1-12 examples 1-3 table 6 claims 1-6  ---  -/--	1-3, 9, 13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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<b>*G*</b> document member of the same patent family		
Date of the actual completion of the international search  19 January 2001		Date of mailing of the international search report  19/02/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Bazzanini, R

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<del>EP 0 619 111 A (NAT STARCH CHEM INVEST)</del> 12 October 1994 (1994-10-12) page 6, line 35 -page 7, line 15 tables 3, 4 -----	1, 3, 4, 6-13
A	FR 2 771 927 A (OREAL) 11 June 1999 (1999-06-11) page 3, line 1-9 page 4, line 9-16 page 4, line 27 -page 5, line 4 page 7, line 8-29 page 8, line 6 -page 12, line 20 claims 1-7, 11, 12, 16, 18 -----	1-13

# INTERNATIONAL SEARCH REPORT

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